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## NASA SEMIANNUAL STATUS REPORT

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TRIFLUOROMETHYL-SUBSTITUTED POLYMERS

July 1, 1993 - December 31, 1993

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## 1.0 Introduction

Current work sponsored by the grant at Southwest Texas State University is directed toward the synthesis and characterization of:

- 1.) N-alkylated polyamides derived from o-fluorinated diacids;
- 2.) Highly fluorinated polyethers;
- 3.) Polyesters derived from 2-hydroxy-2-propyl-substituted arenes and/or 2,5-difluoroterephthalic acid;
- 4.) Silicon-containing fluoropolymers.

The status of each of these projects was summarized in the January 1 - July 1, 1993, Semiannual Status Report. Work during the July 1 - December 31, 1993 period focused primarily on items 3.) and 4.) above, and on the development of a phosphorus containing modification of "12F-PEK." This report focuses on these three areas.

## 2.0 Fluorinated Polyesters

The July - December, 1992 Report disclosed the synthesis of several polyesters derived from 1,3- or 1,4-bis(hexafluoro-2-hydroxy-2-propyl)benzene. Work continues to develop procedures which will yield these compounds reproducibly so that consistent thermal properties can be determined and reported. The data presented in Table 1 summarize the current status of this part of the research. This work will be concluded and published during Spring of 1994.

Work is also proceeding in the synthesis of poly(2,5-difluoroterephthalates) in order to compare their structure property relations to those of analogous terephthalate esters. The dihydroxy compounds being investigated include: 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, oxydiphenol, 4,4'-dihydroxydiphenylsulfone, 1,4-bis(hydroxymethyl)benzene, 1,6-hexanediol, 1,5-pentanediol, 1,4-butanediol and ethylene glycol. Preliminary results with the aliphatic diols indicate the formation of the expected fibrous polyesters ( $\eta_{inh} \approx 0.15 - 0.26$  dL/g). It is anticipated that the difluoroterephthalates will have lower values of  $T_g$  and  $T_m$  than their non-fluorinated analogues and will thus show improved processability.

## 3.0 Silicon-containing Fluoropolymers

We continue to work toward the preparation of new polymers containing both silicon and fluorine. Properly designed polymers have the potential to exhibit resistance to atomic oxygen and ultraviolet radiation and, thus, to be potentially useful as coating materials for low earth orbit applications.

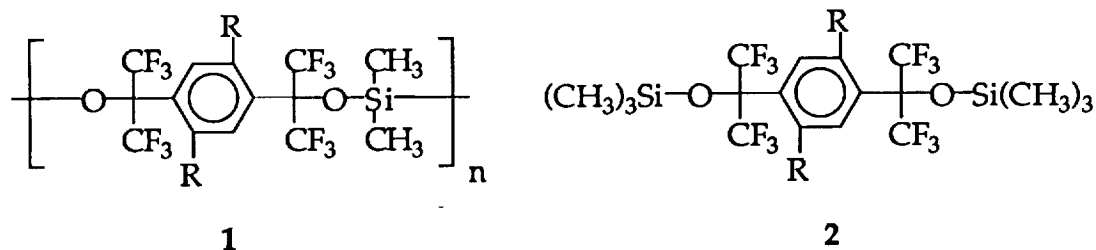
### 3.1 Polysilicates derived from 1,4-HFAB

In our last report we disclosed the synthesis of polysilicate, **1a** ( $R = H$ ), as a moderately stable ( $T_{10\% \text{ Wt. Loss}} = 350^\circ$ ) solid which slowly degrades by hydrolysis in wet polar solvents. Because **2b** ( $R = Si(CH_3)_3$ ), which was also

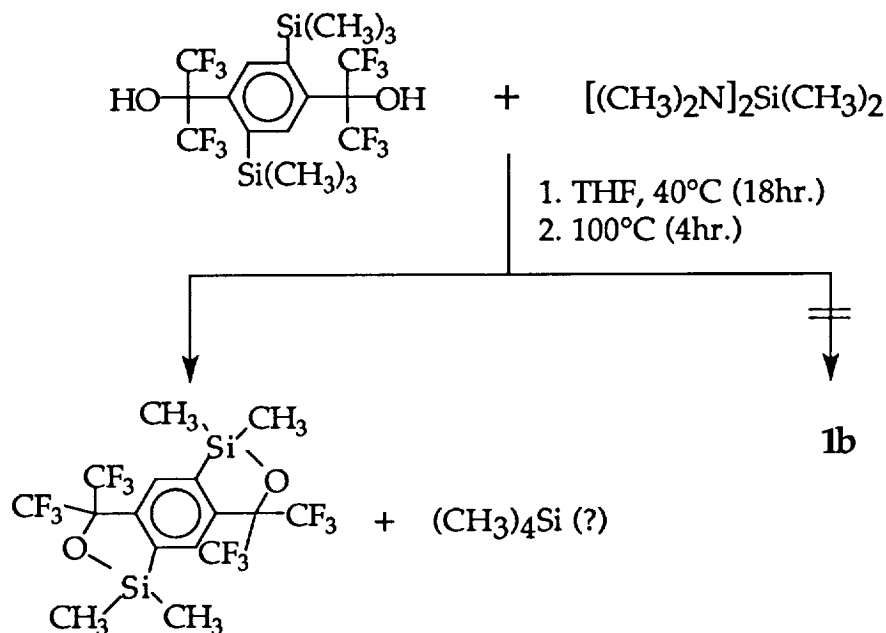
Table 1: Properties of Polyesters

Polyester	%Y	Elemental analyses Cal:Obs	$[\eta]$ dL/g	TGA/N <sub>2</sub> 10%, °C	DSC T <sub>g</sub> , °C
	95	44.44:44.61 %C 1.48:1.63 %H	0.49 <sup>a</sup>	374	*
	1,3- 52	44.44:44.42 %C 1.48:1.72 %H	0.85 <sup>b</sup>	376	115 (110) <sup>d</sup>
	1,4- 40	44.44:44.99 %C 1.48:1.62 %H	0.59 <sup>b</sup>	363	*
	1,3- 27	44.44:44.02 %C 1.48:1.86 %H	0.36 <sup>c</sup>	317	103 <sup>e</sup>
	1,4- 22	44.44:42.63 %C 1.48:2.38 %H	0.23 <sup>c</sup>	361	115 <sup>e</sup>
	1,3- 55	41.69:40.55 %C 1.05:0.8 %H	0.55 <sup>a</sup>	361	171 <sup>e</sup>
	1,4- 49	41.69:40.15 %C 1.05:1.13 %H	0.15 <sup>a</sup>	323	239 <sup>e</sup>
	1,3- 16	45.43:44.33 %C 1.57:1.89 %H	0.29 <sup>c</sup>	400	129 <sup>e</sup>
	1,4- 14	45.43:43.96 %C 1.57:2.34 %H	0.17 <sup>c</sup>	390	155 <sup>e</sup>

a: in DMAc-LiCl<sub>4</sub> (7%), b: in DMAc-LiCl<sub>4</sub> (4%), c: in THF, d: duplicate on second sample,  
e: questionable, synthesis and determination being repeated,  
\*: none observed below 285°C



prepared in our labs at Southwest Texas, is much more resistant to hydrolysis of the Si-O bonds than 2a (R = H), we attempted to prepare polysilicate 1b (R = Si(CH<sub>3</sub>)<sub>2</sub> (Scheme I). Similar thermal ring closures are reported for

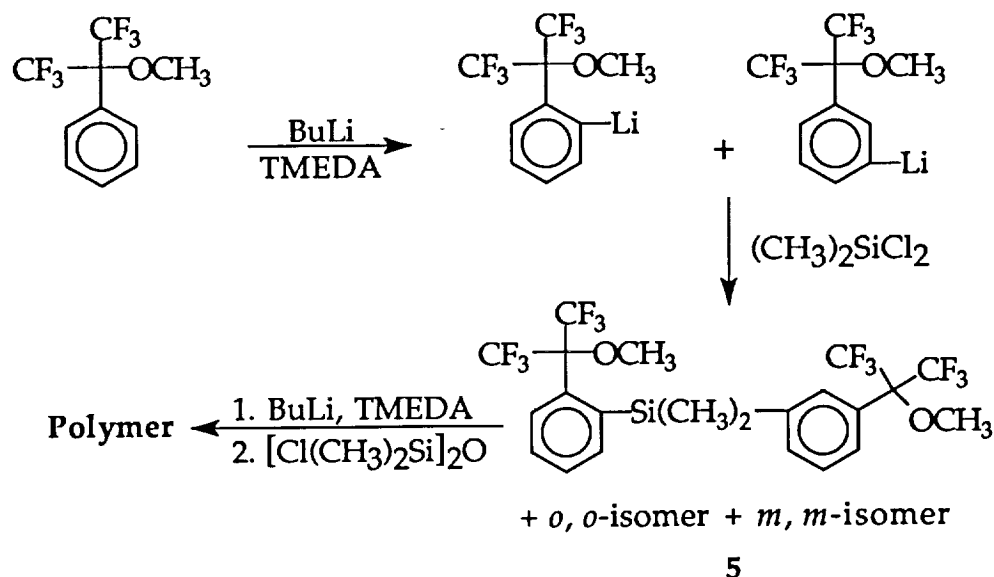


Scheme I

2-(o-trimethylsilylphenyl)hexafluoro-2-hydroxypropane in highly polar aprotic solvents (Yamamoto, *et al.*, Tetra-Lett. 30, 725 (1989)). We conclude from our results that polymers such as 1b, if they form at all, are unstable with respect to thermal degradation. No further work is planned on this type of polymer.

### 3.2 Poly(silphenylene-siloxane)s

For some time we have been working to synthesize fluorinated poly(silphenylene-siloxane)s such as 3 or 4. Both polymers would be accessible from commercially available 1,3- or 1,4 bis(hexafluoro-2-hydroxy-2-propyl)-benzene (1,3 or 1,4-HFAB). The proposed synthesis of 3 and 4 requires that



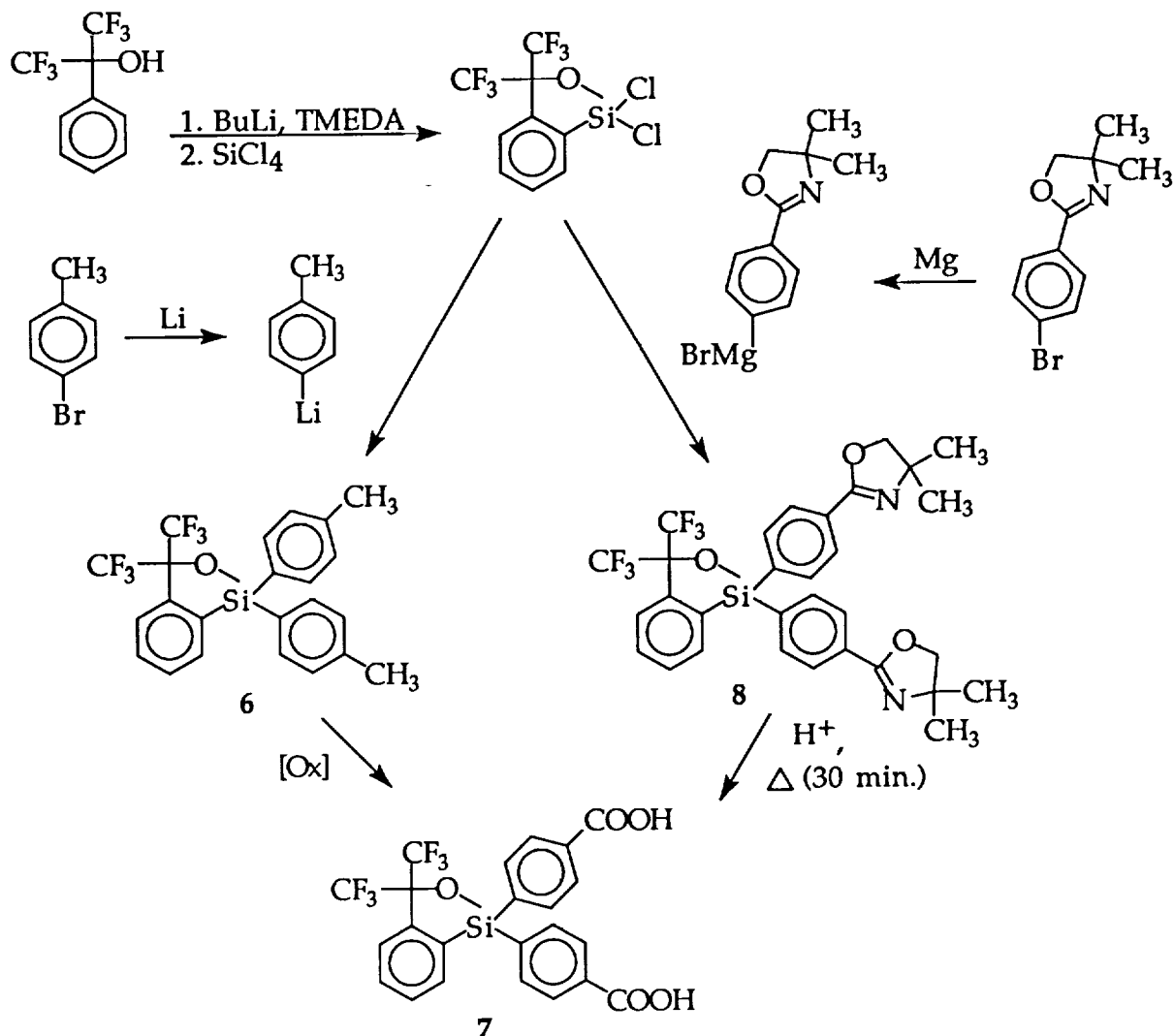
Scheme II

At this time we report the synthesis of 5 which will be used in the proposed polymerization route (Scheme II).

### 3.3 New Monomers

A new silicon-containing compound, 6, has been synthesized from the commercially available HFAB (see Scheme III). This compound is a potential precursor to the new monomer, 7. Several unsuccessful attempts were made to oxidize 6 to 7. We will continue attempting to oxidize 6; however, if the methyl groups do not oxidize before the stable "dihydrobenzoxasilole" ring is destroyed, an alternative route will be used. This route uses the oxazoline, 8, to protect the carboxylic acid function. Oxazolines are known as protecting groups resistant to cleavage by Grignard reagents but which can be easily cleaved in the presence of dilute acid to give the corresponding carboxylic acid. The three major starting materials for this project are in good supply (p-bromotoluene, oxazoline, and HFAB).

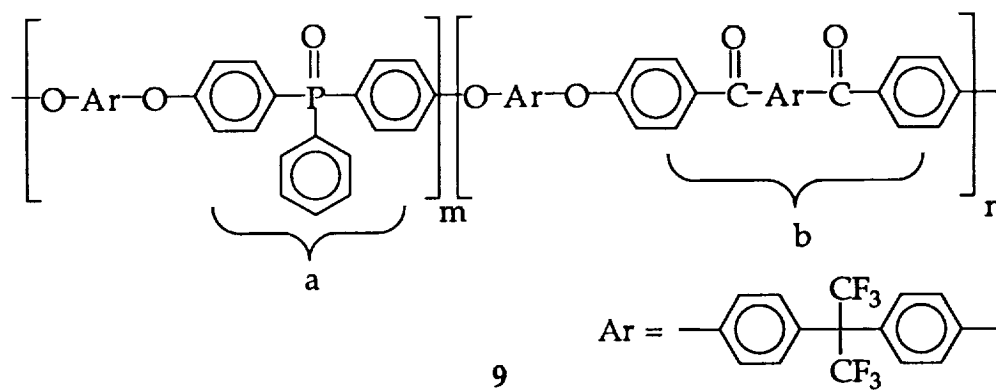
Monomer 7, when prepared will be used to prepare polyesters, polyamides, polyoxadiazoles, etc. containing the "cardo-like" dihydrobenzoxasilole ring in the backbone. Our experience with this ring structure indicates that it is highly resistant to oxidation and to hydrolysis.



Scheme III

#### 4.0 Phosphorus-Containing Modification of 12F-PEK

A phosphorus-containing analogue, 9, of 12F-PEK has been prepared. The average repeat unit is  $\text{C}_{77}\text{H}_{45}\text{F}_{18}\text{O}_7\text{P}$  (FW = 1454) with the phosphorus-containing moiety a (in structure 9) randomly replacing unit b in conventional 12F-PEK. Preliminary results from GPC analysis yield a MW - 64,000 (polystyrene standard) indicating approximately 44 repeating units. The white film-forming solid had an inherent viscosity of 0.28 dL/g and analyzed correctly: Found (Th) C: 63.22% (63.55); H: 2.86% (3.10). A small sample of the new polymer has been submitted to NASA, Langley, for additional evaluation.



Work will continue to improve the synthesis and to determine the effect on bulk polymer properties of varying the amount of phosphorus-containing material in the polymer.